Reactions of ether-phosphine ruthenium hydride complexes with carbon disulfide and phenylacetylene: crystal structures of RuCl(P ~ O)$_3$(η^2-S$_2$CH) and Ru(CO)Cl(P ~ O)$_2$(η^2-S$_2$CH) [1]

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Abstract

The dithioformato complexes RuCl(P ~ O)$_3$(η^2-S$_2$CH) (2a,b) and RuCl(P ∩ O)(P ~ O)(η^2-S$_2$CH) (3a,b) are accessible by insertion of CS$_2$ into the Ru–H bond of the (ether-phosphine)(hydrido)ruthenium complexes RuClH(P ∩ O)(P ~ O)$_2$ (1a,b) [P ~ O = η^1(P)-coordinated, P ∩ O = η^2(O,P)-chelated; O,P = diphenyl(2-methoxyethyl)phosphine (a), (1,3-dioxan-2-ylmethyl) diphenylphosphine (b)]. Treatment of 2a, 3a and 2b, 3b with carbon monoxide in CH$_2$Cl$_2$ results in the formation of the carbonyl complexes Ru(CO)Cl(P ~ O)$_2$(η^2-S$_2$CH) (4a,b). The structures of 2a and 4a were determined by single crystal X-ray diffraction analyses. Crystal data for 2a: space group Pca2$_1$ with a = 17.578(4) Å, b = 14.215(3) Å, c = 17.934(4) Å, V = 4481(2) Å^3, Z = 4. The structure was refined to R = 0.037, wR = 0.082. Crystal data for 4a: space group P2$_1$/n with a = 12.009(2) Å, b = 17.143(4) Å, c = 16.510(4) Å, β = 107.92(2)°, V = 3234(1) Å^3, Z = 4. The structure was refined to R = 0.035, wR = 0.087. 1a,b react with phenylacetylene to give the acetylide complexes RuCl(P ∩ O)$_2$(C≡CPh) (5a,b) with evolution of dihydrogen. Carbonylation of 5a yields the cis-η^1(P)-coordinated complex RuCl(CO)$_2$(P ~ O)$_2$(C≡CPh) (6). If chloride is abstracted from Ru(CO)Cl(P ~ O)$_2$(η^2-S$_2$CH) (4a) with AgBF$_4$ in THF the P ∩ O-chelated complex [Ru(CO)(P ∩ O)(P ~ O)(η^2-S$_2$CH)][BF$_4$] (7) is obtained. Upon reaction of 7 with PhC≡CH the Ru–O bond is cleaved and instead of an η^1-vinylidene species the acetylide complex Ru(CO)(P ~ O)$_2$(η^2-S$_2$CH)(C≡CPh) (8) is formed.

Keywords: Ruthenium; Hydride; Ether-phosphine; Carbon disulfide; Phenylacetylene; Hydrogen bonding; Crystal structure; Group 8

1. Introduction

Recently we reported on the synthesis, reactivity and dynamic behavior of some transition metal complexes containing hemilabile ether-phosphines (O,P) [1]. These systems, in which the ether oxygen atom is incorporated in open-chain or cyclic ether moieties, act as monodentate (P ~ O = η^1(P)-coordinated) or bidentate (P ∩ O = η^2(O,P)-coordinated) ligands. The ether oxygen atom is able to stabilize coordinatively unsaturated metal complexes by formation of weak metal–oxygen bonds, and the ether part of this type of ligand is regarded as an intramolecular solvent [2]. The metal–oxygen bond strength depends on the ring size, number, position and

nucleophilicity of the ether oxygen atoms, and the basicity of the metal center [3]. In reactions of chelated (ether-phosphine)metal complexes with some small molecules such as sulfur dioxide, ethene, carbon monoxide, carbon disulfide, and phenylacetylene the metal–oxygen bond is easily cleaved to form the substituted complexes that have been reported by us recently [4].

The reactions of carbon disulfide and phenylacetylene with transition metal complexes have attracted a great deal of attention in recent years, owing mainly to their potential as sources of C1 chemistry in organic synthesis [5], and as catalysts for polymerization and hydrogenation of alkynes [6].

The cleavage of the weak metal–oxygen bond in (ether-phosphine)metal complexes enables the addition of small molecules under very mild conditions. Herein we describe the reactions of an (ether-phosphine)(hy-

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drido)ruthenium complex with carbon disulfide, carbon monoxide and phenylacetylene to form ruthenium complexes containing dithioformato, carbonyl and phenylacetylide groups.

2. Experimental section

2.1. Materials

All manipulations were performed under argon using vacuum-line and standard Schlenk techniques. Solvents were dried and deoxygenated by refluxing over the appropriate reagents prior to use. n-Hexane, diethyl ether, tetrahydrofuran and benzene were distilled from sodium/ benzophenone. Acetonitrile and dichloromethane were distilled from calcium hydride, and methanol from magnesium. IR spectra were measured on a Bruker IFS 48 instrument and were referenced to a polystyrene standard, using cells equipped with sodium chloride windows. FAB mass spectra were recorded on a Finnigan MAT TSQ 70 (10 kV, 50 °C) spectrometer. Elemental analyses were performed with a Carlo Erba 1106 analyzer; Cl and S analyses were carried out according to Schöniger [7] and analyzed as described by Dirschel and Erne [8] and Wagner [9]. Ru was determined according to the literature [10]. $^{31}P\{^{1}H\}$ NMR spectra were obtained on a Bruker WP 80 and a Bruker DRX 250 spectrometer operating at 32.39 and 101.25 MHz respectively, external standard (coaxial insert) 1% H_3PO_4 in acetone-d_6 for $T \leq 273$ K. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were measured with Bruker DRX 250 and Bruker AMX 400 spectrometers at 250.13 and 62.90, 400.13 and 100.62 MHz respectively. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to TMS. All other solvents and reagents were of reagent grade and were used as-received. $RuCl_3$, $PhC\equiv CH$ and CS_2 were purchased from Heraeus, Merck and Riedel-de Haën respectively. The starting complexes $RuClH(P \cap O)(P \sim O)_2$ (**1a,b**) were synthesized as previously described [11].

2.2. Chloro-tris[diphenyl(2-methoxyethyl)phosphine-P](η^2-dithioformato)ruthenium(II) (2a) and chloro-bis[diphenyl(2-methoxyethyl)phosphine-P;O',P']η^2-dithioformato)ruthenium(II) (3a)

A solution of $RuClH(P \cap O)(P \sim O)_2$ (**1a**) (400 mg, 0.46 mmol) in 20 ml of n-hexane was treated with carbon disulfide (126 mg, 1.65 mmol) at ambient temperature. Instantaneously the reaction mixture turned to orange–red. After 10 min of stirring an orange–red precipitate was formed. The precipitate was collected by filtration (G4) and dried in vacuo. Further purification was accomplished by recrystallization from a mixture of

CH_2Cl_2/n-hexane (1:10). Analysis of the spectral data showed a mixture of the two complexes **2a** and **3a**. The ratio **2a/3a** of ca. 4:3 was obtained by integration of the absorptions in the $^{31}P\{^{1}H\}$ NMR spectrum. Overall yield 329 mg (85%). When n-hexane was slowly diffused into a CH_2Cl_2 solution of a mixture of **2a** and **3a** different shaped crystals of these compounds were obtained, which could be separated mechanically for analytic characterization. Spectroscopic data of **2a**: m.p. 141–143 °C (dec.). Anal. Found: C, 58.38; H, 5.38; Cl, 3.80; Ru, 10.62; S, 6.76. $C_{46}H_{52}ClO_3P_3RuS_2$. Calc.: C, 58.37; H, 5.54; Cl, 3.75; Ru, 10.68; S, 6.78%. IR (KBr): δ(HCS) 1225 (m), $\nu_{as}(CS_2)$ 907 (m) cm^{-1}. $^{31}P\{^{1}H\}$ NMR (101.25 MHz, CDCl$_3$, 298 K): δ 22.6 (t, ^2J(PP) 30.5 Hz, P$^1 \sim$ O), 20.1 (d, ^2J(PP) 30.5 Hz, P$^{2,3} \sim$ O). ^{1}H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 10.29 (dt, ^4J(PH) 5.1, ^4J(PH) 3.6 Hz, 1 H, HCS$_2$), 7.65–6.70 (m, 30 H, Ph), 3.68–3.01 (m, 12 H, PCH$_2$CH$_2$), 2.82 (s, 9 H, OCH$_3$). $^{13}C\{^{1}H\}$ NMR (100.62 MHz, CDCl$_3$, 298 K): δ 230.3 (s, CS$_2$), 138.3–126.4 (m, C–Ph), 69.2, 67.9 (s, PCH$_2$CH$_2$), 57.9, 57.5 (s, OCH$_3$), 26.3 (m, PCH$_2$). MS [FAB, 3-nitrobenzyl-alcohol (NOBA)] m/e 945.6 [M$^+$], 910.4 [M$^+$–Cl]. Spectroscopic data of **3a**: m.p. 138–140 °C (dec.). Anal. Found: C, 53.24; H, 4.72; Cl, 5.09; Ru, 14.74; S, 9.33. $C_{31}H_{35}ClO_2P_2RuS_2$. Calc.: C, 53.02; H, 5.02; Cl, 5.05; Ru, 14.39; S, 9.13%. IR (KBr): δ(HCS) 1226 (m), $\nu_{as}(CS_2)$ 907 (m) cm^{-1}. $^{31}P\{^{1}H\}$ NMR (101.25 MHz, CDCl$_3$, 298 K): δ 49.6 (d, ^2J(PP) 30.4 Hz, P $\cap$ O), 46.2 (d, ^2J(PP) 30.4 Hz, P $\sim$ O). ^{1}H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 11.62 (dd, ^4J(PH) 3.0, ^4J(PH) 2.0 Hz, 1 H, HCS$_2$), 8.07–6.58 (m, 20 H, Ph), 3.53–2.62 (m, 8H, PCH$_2$CH$_2$). $^{13}C\{^{1}H\}$ NMR (100.62 MHz, CDCl$_3$, 298 K): δ 239.9 (s, CS$_2$). MS (FAB, NOBA) m/e 701.4 [M$^+$], 667.3 [M$^+$–Cl].

2.3. Chloro-tris[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P](η^2-dithioformato)ruthenium(II) (2b) and chloro-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P;O',P'](η^2-dithioformato)ruthenium(II) (3b)

A solution of $RuClH(P \cap O)(P \sim O)_2$ (**1b**) (400 mg, 0.401 mmol) in 20 ml of diethyl ether was treated with carbon disulfide (126 mg, 1.65 mmol) at room temperature. Instantaneously the reaction mixture turned to orange–red. The solution was concentrated under vacuum to give an orange–red precipitate. The precipitate was collected by filtration (G4) and dried in vacuo. Analysis of the spectral data showed a mixture of the complexes **2b** and **3b**. The ratio **2b/3b** of ca. 1:18 was obtained by integration of the absorptions in the $^{31}P\{^{1}H\}$ NMR spectrum. Overall yield 295 mg (92%). Spectroscopic data of **2b**: because of the low yield, **2b** could not be separated from **3b**, therefore an elemental analysis of **2b** was not available. $^{31}P\{^{1}H\}$ NMR (101.25 MHz, CDCl$_3$, 298 K): δ 24.6 (t, ^2J(PP) 26.3 Hz,

$P^1 \sim O$), 21.5 (d, ^2J(PP) 26.3 Hz, $P^{2,3} \sim O$). ^1H (400.13 MHz, CDCl$_3$, 298 K): δ 10.17 (dt, ^4J(PH) 4.8, ^4J(PH) 3.6 Hz, 1 H, HCS$_2$), 8.22–6.81 (m, 30 H, Ph), 4.81–1.00 (m, 27 H, alkanes). $^{13}C\{^1H\}$ NMR (100.62 MHz, CDCl$_3$, 298 K): δ 137.2–125.1 (m, C–Ph), 104.4 (d, ^2J(PC) 14.1 Hz, PCH$_2$CH), 66.9 (s, OCH_2CH$_2$), 35.1 (m [12], J(PC) 17.1 Hz, PCH$_2$), 25.4 (s, OCH$_2$CH_2). Spectroscopic data of **3b**: m.p. 110–112 °C (dec.). Anal. Found: C, 53.55; H, 5.19; Cl, 5.13; Ru, 12.97; S, 7.81 [1]. C$_{35}$H$_{39}$ClO$_4$P$_2$RuS$_2$. Calc.: C, 53.46; H, 5.00; Cl, 4.51; Ru, 12.85; S, 8.16%. IR (KBr) δ(HCS) 1243 (m), ν_{as}(CS$_2$) 928 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, CDCl$_3$, 298 K): δ 44.5 (d, ^2J(PP) 31.5 Hz, P $\cap$ O), 22.6 (d, ^2J(PP) 31.5 Hz, P $\sim$ O). ^1H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 11.68 (dd, ^4J(PH) 5.1, ^4J(PH) 3.6 Hz, 1 H, HCS$_2$), 7.89–6.22 (m, 20 H, Ph), 4.47–0.59 (m, 18 H, alkanes). $^{13}C\{^1H\}$ NMR (100.62 MHz, CDCl$_3$, 298 K): δ 239.8 (s, CS$_2$), 138.7–126.5 (m, C–Ph), 100.6 (d, ^2J(PC) 20.1 Hz, PCH$_2$CH, P $\cap$ O), 100.3 (d, ^2J(PC) 5.0 Hz, PCH$_2$CH, P $\sim$ O), 67.4 (m, OCH_2CH$_2$, P $\cap$ O), 66.4 (m, OCH_2CH$_2$, P $\sim$ O), 37.8 (m [12], J(PC) 26.2 Hz, PCH$_2$, P $\cap$ O), 35.1 (m [12], J(PC) 17.1 Hz, PCH$_2$, P $\sim$ O), 26.3 (s, OCH$_2$CH_2, P $\cap$ O), 25.1 (s, OCH$_2$CH_2, P $\sim$ O). MS (FAB, NOBA) m/e 786.6 [M$^+$], 751.6 [M$^+$–Cl], 673.7 [M$^+$–Cl–HCS$_2$].

2.4. Carbonyl(chloro)-bis[diphenyl(2-methoxyethyl)phosphine-P](η²-dithioformato)ruthenium(II) (4a)

Carbon monoxide was bubbled for 10 min into a stirred solution of a 4:3 mixture of **2a** (171 mg, 0.181 mmol) and **3a** (129 mg, 0.184 mmol) in 20 ml of dichloromethane at ambient temperature. A color change from red to yellow occurred within 5 min. Subsequently the solvent was removed under vacuum. The residue was redissolved in 5 ml of CH$_2$Cl$_2$. *n*-Hexane (15 ml) was added to the solution and a yellow precipitate was formed. The precipitate was collected by filtration (G4) washed with *n*-hexane (2 × 10 ml) and then dried in vacuo yielding 253 mg (95%) of **4a**; m.p. 157–159 °C (dec.). Anal. Found: C, 52.64; H, 5.18; Cl, 4.90; Ru, 13.92; S, 8.73. C$_{32}$H$_{35}$ClO$_3$P$_2$RuS$_2$. Calc.: C, 52.63; H, 4.83; Cl, 4.85; Ru, 13.84; S, 8.78%. IR (KBr): ν(CO) 1946 (vs) cm^{-1}, δ(HCS) 1226 (m), ν_{as}(CS$_2$) 924 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, CDCl$_3$, 298 K): δ 24.7. ^1H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 10.40 (t, ^4J(PH) 3.5 Hz, 1 H, HCS$_2$), 7.75–7.04 (m, 20 H, Ph), 3.72–3.54 (m, 8 H, PCH$_2$CH$_2$), 3.40 (s, 6 H, OCH$_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, CDCl$_3$, 298 K): δ 232.1 (t, ^3J(PC) 5.0 Hz, CS$_2$), 202.5 (t, ^2J(PC) 12.1 Hz, CO), 133.9–127.6 (m, C–Ph), 68.2 (s, PCH$_2$CH_2),

58.2 (s, OCH$_3$), 27.0 (m [12], J(PC) 13.8 Hz, PCH$_2$). MS (FAB, NOBA) m/e 730.5 [M$^+$], 695.5 [M$^+$–Cl], 667.5 [M$^+$–Cl–CO].

2.5. Carbonyl(chloro)-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-P](η²-dithioformato)ruthenium(II) (4b)

Carbon monoxide was bubbled for 5 min into a stirred solution of a 1:18 mixture of **2b** (16 mg, 0.015 mmol) and **3b** (284 mg, 0.361 mmol) in 20 ml of dichloromethane at ambient temperature. A spontaneous color change from red to yellow occurred. Subsequently the solvent was removed under vacuum. The residue was washed with 10 ml of *n*-hexane to give a yellow precipitate, which was collected by filtration (G4) and dried in vacuo to yield 300 mg (98%) of **4b**; m.p. 151–153 °C (dec.). Anal. Found: C, 53.17; H, 5.09; Cl, 4.56; Ru, 12.72; S, 7.01. C$_{36}$H$_{39}$ClO$_5$P$_2$RuS$_2$. Calc.: C, 53.10; H, 4.83; Cl, 4.35; Ru, 12.41; S, 7.88%. IR (KBr): ν(CO) 1947 (vs) cm^{-1}, δ(HCS) 1227 (m), ν_{as}(CS$_2$) 927 (m) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, CDCl$_3$, 298 K): δ 25.1. ^1H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 10.50 (t, ^4J(PH) 3.5 Hz, 1 H, HCS$_2$), 7.82–7.03 (m, 20 H, Ph), 4.34–0.81 (m, 18 H, alkanes). $^{13}C\{^1H\}$ NMR (100.62 MHz, CDCl$_3$, 298 K): δ 231.8 (t, ^3J(PC) 5.2 Hz, CS$_2$), 202.7 (t, ^2J(PC) 12.4 Hz, CO), 134.2–127.2 (m, C–Ph), 99.9 (s, PCH$_2$CH), 66.7, 66.4 (s, OCH_2CH$_2$), 32.5 (m [12], J(PC) 15.1 Hz, PCH$_2$), 25.2 (s, OCH$_2$CH_2). MS (FAB, NOBA) m/e 737.6 [M$^+$–HCS$_2$], 637.2 [M$^+$–HCS$_2$–Cl–CO].

2.6. Chloro-bis[diphenyl(2-methoxyethyl)phosphine-O,P](phenylacetylido)ruthenium(II) (5a)

Addition of phenylacetylene (46 mg, 0.45 mmol) to a solution of **1a** (400 mg, 0.46 mmol) in 20 ml of diethyl ether, followed by a short period of stirring at room temperature, gave a yellow solution which was concentrated to 5 ml. Upon cooling the solution below 0 °C, a yellow precipitate was obtained which was isolated by filtration (G4) and washed with *n*-hexane (2 × 10 ml) and subsequently dried under vacuum to yield 240 mg (72%) of **5a**; m.p. 100–102 °C (dec.); Anal. Found: C, 62.54; H, 5.76; Cl, 4.72; Ru, 13.68. C$_{38}$H$_{39}$ClO$_2$P$_2$Ru. Calc.: C, 62.84; H, 5.41; Cl, 4.88; Ru, 13.92%. IR (KBr): ν(C≡C) 2064 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (32.39 MHz, CH$_2$Cl$_2$, 248 K): δ 23.5. ^1H NMR (400.13 MHz, CDCl$_3$, 298 K): δ 7.50–7.10 (m, 25 H, Ph), 3.87 (s, 4 H, PCH$_2$CH_2), 3.30 (s, 6 H, OCH$_3$), 2.71 (m, 4 H, PCH$_2$). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K): δ 134.2–127.3 (m, C–Ph), 110.4 (br s, PhC), 108.6 (br s, RuC), 70.0 (m, PCH$_2$CH_2), 59.2 (s, OCH$_3$), 30.7 (m, PCH$_2$). MS (FAB, NOBA) m/e 726.1 [M$^+$], 691.1 [M$^+$–Cl], 589.1 [M$^+$–Cl–PhC$_2$].

[1] The elemental analysis was obtained from a 1:18 mixture of **2b/3b**.

2.7. Chloro-bis[(1,3-dioxan-2-ylmethyl)diphenylphosphine-O,P](phenylacetylido)ruthenium(II) (5b)

To a yellow solution of **1b** (400 mg, 0.401 mmol) in 10 ml of diethyl ether was added phenylacetylene (93 mg, 0.91 mmol) at room temperature. After 5 min of stirring the solvent was removed under vacuum and was washed with 10 ml of n-hexane to give a yellow precipitate. The precipitate was collected by filtration (G4) and dried in vacuo to yield 293 mg (90%) of **5b**; m.p. 105–107 °C (dec.). Anal. Found: C, 62.26; H, 5.85; Cl, 4.40; Ru, 12.84. $C_{42}H_{43}ClO_4P_2Ru$. Calc.: C, 62.25; H, 5.35; Cl, 4.38; Ru, 12.47%. IR (KBr) $\nu(C\equiv C)$ 2065 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (32.39 MHz, CH_2Cl_2, 248 K): δ 44.3 (d, $^2J(PP)$ 47.0 Hz), 32.6 (d, $^2J(PP)$ 47.0 Hz). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 298 K): δ 137.1–122.1 (m, C–Ph), 104.7 (br s, PhC), 104.2 (br s, RuC), 100.6, 100.4 (s, PCH_2CH), 66.9, 66.7, 66.5, 65.8 (s, OCH_2CH_2), 38.0, 36.4 (m, PCH_2), 25.9, 24.7 (each s, OCH_2CH). MS (FAB, NOBA) m/e 809.7 $[M^+]$, 775.7 $[M^+–Cl]$, 673.7 $[M^+–Cl–PhC_2]$.

2.8. Chloro(dicarbonyl)-bis[diphenyl(2-methoxyethyl)phosphine-P](phenylacetylido)ruthenium(II) (6)

Carbon monoxide was bubbled for 15 min into a stirred solution of **5a** (200 mg, 0.275 mmol) in 20 ml of diethyl ether at room temperature. Subsequently the solvent was removed under vacuum. The residue was washed with 10 ml of n-hexane to give a yellow precipitate, which was collected by filtration (G4) and dried in vacuo to yield 200 mg (93%) of **6**; m.p. 140–142 °C (dec.). Anal. Found: C, 60.97; H, 5.52; Cl, 4.97; Ru, 12.51. $C_{40}H_{39}ClO_4P_2Ru$. Calc.: C, 61.41; H, 5.02; Cl, 4.53; Ru, 12.92%. IR (KBr): $\nu(C\equiv C)$ 2047 (m) cm^{-1}, $\nu(CO)$ 1989 (vs), 1942 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 298 K): δ 16.7. ^1H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 8.17–7.04 (m, 25 H, Ph), 3.75–3.41 (m, 8 H, PCH_2CH_2), 3.14 (s, 6 H, OCH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 298 K): δ 113.4 (br s, PhC), 110.2 (br s, RuC), 67.8 (s, PCH_2CH_2), 58.1 (s, OCH_3), 26.7 (m, PCH_2). MS (FAB, NOBA) m/e 753.4 $[M^+–CO]$, 726.6 $[M^+–2CO]$.

2.9. Carbonyl-bis[diphenyl(2-methoxyethyl)phosphine-P;O′,P′](η²-dithioformato)ruthenium(II) tetrafluoroborate (7)

A mixture of **4a** (197 mg, 0.27 mmol) and $AgBF_4$ (53 mg, 0.27 mmol) dissolved in 15 ml of tetrahydrofuran was stirred for 5 h. The solution was stirred and monitored by $^{31}P\{^1H\}$ NMR. After complete disappearance of the $^{31}P\{^1H\}$ resonance of complex **4a** the reaction was finished and the solution was filtered through Celite. The filtrate was dried in vacuo to yield 172 mg

(82%) of **7** as a yellow oil. IR (CH_2Cl_2): $\nu(CO)$ 1987 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (32.39 MHz, THF, 248 K): δ 46.0 (d, $^2J(PP)$ 240.0 Hz, P $\cap$ O), 18.3 (d, $^2J(PP)$ 240.0 Hz, P $\sim$ O). ^1H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 12.17 (pseudo t, $^4J(PH)$ 6.4 Hz, 1 H, HCS_2), 7.54–7.13 (m, 20 H, Ph), 3.74–3.36 (m, 8 H, PCH_2CH_2). $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_3COCD_3, 298 K): δ 233.2 (s, CS_2), 203.5 (br s, CO), 134.9–128.2 (m, C–Ph), 69.3 (s, PCH_2CH_2), 58.9 (s, OCH_3), 28.9 (m [12], $J(PC)$ 5.0 Hz, PCH_2). MS (FAB, NOBA) m/e 694.7 $[M^+–BF_4]$.

2.10. Carbonyl-bis[diphenyl(2-methoxyethyl)phosphine-P](η²-dithioformato)(phenylacetylido)ruthenium(II) (8)

Phenylacetylene (0.46 mg, 0.45 mmol) was added to a solution of **7** (200 mg, 0.257 mmol) in 5 ml of tetrahydrofuran and 10 ml of methanol. The solution was stirred for 3 days and a yellow precipitate was formed. The precipitate was collected by filtration (G4) and dried in vacuo. Yield 159 mg (78%) of **8**; m.p. 152–154 °C (dec.); Anal. Found: C, 59.91; H, 5.22; Ru, 12.78; S, 8.04. $C_{40}H_{41}O_3P_2RuS_2$. Calc.: C, 60.28; H, 5.19; Ru, 12.68; S, 8.05%. IR (KBr): $\nu(C\equiv C)$ 2120 (m) cm^{-1}, $\nu(CO)$ 1940 (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 298 K): δ 18.3 (s). ^1H NMR (400.13 MHz, $CDCl_3$, 298 K): δ 10.39 (t, $^4J(PH)$ 3.5 Hz, 1 H, HCS_2), 7.93–7.09 (m, 25 H, Ph), 3.62–3.41 (m, 8 H, PCH_2CH_2), 3.19 (s, 6 H, OCH_3). $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$, 298 K): δ 236.3 (t, $^3J(PC)$ 5.2 Hz, CS_2), 202.2 (t, $^2J(PC)$ 13.1 Hz, CO), 133.4–124.2 (m, C–Ph), 113.0 (br s, PhC), 110.0 (t, $^2J(PC)$ 17.7 Hz, RuC), 68.1 (s, PCH_2CH_2), 57.9 (s, OCH_3), 29.1 (m [12], $J(PC)$ 15.0 Hz, PCH_2). MS (FAB, NOBA) m/e 795.5 $[M^+]$, 695.2 $[M^+–PhC_2]$.

2.11. Structure determination of 2a and 4a

Crystal data and details of data collection are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for **2a** and **4a** are given in Tables 2 and 3. Single crystals were obtained by slow diffusion of n-hexane into concentrated CH_2Cl_2 solutions of **2a** and **4a** respectively. All crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer taking rotation photographs and performing a photo search to find a suitable reduced cell (graphite-monochromated Mo K α radiation).

The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. All structures were solved by Patterson methods [13] and refined by least-squares with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were included in calculated positions (riding model). For complex **2a** the Flack parameter was determined [−0.04(3)]. An absorption

Table 1

Crystal data and collection parameters for **2a** and **4a**

	2a	4a
Formula	$C_{46}H_{52}ClO_3P_3RuS_2$	$C_{32}H_{35}ClO_3P_2RuS_2$
FW	946.43	730.18
Crystal size (mm³)	0.10×0.30×0.40	0.30×0.30×0.35
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/n$
a (Å)	17.578(4)	12.009(2)
b (Å)	14.215(3)	17.143(4)
c (Å)	17.934(4)	16.510(4)
β (°)		107.92(2)
V (Å³)	4481(2)	3234(1)
Z	4	4
Calc. density (g cm⁻³)	1.403	1.500
h, k, l range	20, −16 → 13, ±21	±14, 20, ±19
T (°C)	−100	−100
$F(000)$ (e)	1960	1496
μ(Mo Kα) (mm⁻¹)	0.649	0.827
Scan range (2θ)	4–50	4–50
Reflections collected	14927	11390
No. of unique reflections	7891	5700
Obs. data [$I > 2\sigma(I)$]	6358	4480
No. of parameters	507	371
Goodness of fit	1.432	1.573
$R1$ [a]	0.037	0.035
wR_2 [b]	0.082	0.087

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\}/\{\Sigma[w(F_o^2)^2]\}^{0.5}$.

correction ψ-scan was applied to all structures. Maximum and minimum peaks in the final difference synthesis were 0.94 and −0.58 (**2a**), and 1.25 and −0.74 (**4a**) eÅ⁻³ respectively. Because of disorder the displacement parameters of C(30) are very high. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the despository number CSD-58961, the names of the authors and the journal citation.

3. Results and discussion

3.1. Insertion of CS_2 into the Ru–H bond of the complexes $RuClH(P \cap O)(P \sim O)_2$ (1a,b)

Treatment of the starting compounds RuClH(P ∩ O)(P ∼ O)₂ (**1a,b**) [P ∼ O = diphenyl(2-methoxy-ethyl)phosphine (**a**), (1,3-dioxan-2-ylmethyl)diphenyl-phosphine (**b**)] with CS_2 afforded mixtures of the air-stable and orange–red complexes RuCl(P ∼ O)₃(η^2-

S_2CH) (**2a,b**) and RuCl(P ∩ O)(P ∼ O)(η^2-S_2CH) (**3a,b**) with ratios of 4:3 and 1:18 respectively (Scheme 1). From this ratio, it can be derived that the steric

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2a**

Atom	x	y	z	U_{eq}
Ru(1)	9489(1)	8201(1)	2321(1)	17(1)
Cl(1)	8962(1)	8117(1)	1038(1)	25(1)
S(1)	9747(1)	8507(1)	3569(1)	25(1)
S(2)	8545(1)	9326(1)	2799(1)	26(1)
P(1)	10531(1)	7167(1)	2254(1)	21(1)
P(2)	10118(1)	9611(1)	1933(1)	20(1)
P(3)	8511(1)	7085(1)	2646(1)	20(1)
O(1)	10797(3)	5061(5)	3829(4)	82(2)
O(2)	9353(3)	11980(4)	976(3)	82(2)
O(3)	6281(2)	7173(3)	2000(2)	39(1)
C(1)	11536(3)	7719(4)	3396(3)	27(1)
C(2)	12205(3)	8072(4)	3695(3)	32(1)
C(3)	12769(3)	8413(4)	3232(3)	37(1)
C(4)	12659(3)	8388(4)	2465(3)	34(2)
C(5)	11998(3)	8019(3)	2165(2)	26(1)
C(6)	11424(2)	7663(3)	2628(3)	22(1)
C(7)	11576(3)	6081(5)	1398(4)	42(2)
C(8)	11840(4)	5681(6)	754(4)	59(2)
C(9)	11434(4)	5734(6)	106(4)	57(2)
C(10)	10733(4)	6206(5)	93(4)	48(2)
C(11)	10467(3)	6630(4)	745(3)	32(1)
C(12)	10884(3)	6573(4)	1403(3)	28(1)
C(13)	10400(3)	6178(4)	2919(3)	31(1)
C(14)	11057(3)	5546(4)	3167(4)	39(1)
C(15)	11339(4)	4613(7)	4235(4)	76(3)
C(16)	11595(3)	10187(4)	1431(3)	33(1)
C(17)	12192(3)	10159(4)	922(3)	38(1)
C(18)	12160(3)	9550(5)	318(4)	45(2)
C(19)	11533(3)	8983(4)	207(3)	36(1)
C(20)	10935(3)	9005(4)	714(3)	27(1)
C(21)	10965(3)	9597(4)	1328(3)	27(1)
C(22)	9915(3)	11175(4)	2899(3)	32(1)
C(23)	10073(5)	11675(5)	3547(4)	45(2)
C(24)	10677(4)	11450(5)	3991(3)	47(2)
C(25)	11143(4)	10700(5)	3789(3)	45(2)
C(26)	11000(3)	10159(4)	3153(3)	34(1)
C(27)	10377(3)	10392(4)	2701(3)	27(1)
C(28)	9496(3)	10335(4)	1339(3)	28(1)
C(29)	9870(4)	11232(4)	1035(4)	39(1)
C(30)	8979(8)	12113(12)	323(5)	200(11)
C(31)	8765(3)	6565(5)	4136(3)	38(1)
C(32)	8686(4)	6660(6)	4905(3)	53(2)
C(33)	8122(5)	7228(6)	5178(4)	64(2)
C(34)	7616(4)	7676(5)	4703(4)	51(2)
C(35)	7707(3)	7588(4)	3942(3)	35(1)
C(36)	8284(3)	7042(4)	3645(3)	26(1)
C(37)	8855(3)	5614(4)	1676(3)	32(1)
C(38)	8903(3)	4671(5)	1446(4)	42(1)
C(39)	8650(3)	3959(4)	1911(4)	41(1)
C(40)	8344(3)	4173(4)	2603(4)	40(1)
C(41)	8297(3)	5097(4)	2837(3)	33(1)
C(42)	8559(2)	5828(3)	2377(3)	26(1)
C(43)	7604(2)	7415(4)	2196(3)	26(1)
C(44)	6939(2)	6747(3)	2288(4)	29(1)
C(45)	5651(3)	6622(4)	2037(4)	49(2)
C(46)	9005(3)	9234(4)	3624(3)	28(1)

effect of the cyclic ether-phosphine ligand controls the formation of complex **3b**. **2a,b** and **3a,b** are moderately soluble in CH_2Cl_2 and $CHCl_3$, slightly soluble in acetone and tetrahydrofuran, and insoluble in diethyl ether and *n*-hexane. In the FAB mass spectrum, two parent peaks with the typical Ru isotope distribution are in agreement with the molecular masses of **2a** and **3a** respectively. Because of the low yield of complex **2b**, in the FAB mass spectrum of a mixture of **2b** and **3b** only the parent peak corresponding to **3b** appears. The ^1H NMR spectra of mixtures of **2a**, **3a** and **2b**, **3b** respectively display the proton resonances of the dithioformato groups as a doublet of triplets and a doublet of doublets respectively. The former resonance is traced back to two chemically equivalent $\eta^1(P)$-coordinated phosphine molecules $P^2 \sim O$, $P^3 \sim O$ and another $\eta^1(P)$-coordinated phosphine ligand $P^1 \sim O$ and stems from compounds **2a,b**. The latter resonance results from two inequivalent phosphorus atoms in the spectrum of **3a,b**. In the $^{31}P\{^1H\}$ NMR spectrum of the mixtures of **2a**, **3a** and **2b**, **3b** respectively, two sets of resonances are clearly distinguishable. The triplet and the doublet with a ratio of 1:2 are assigned to the $P^1 \sim O$ ligand and to the two chemically equivalent $P^2 \sim O$ and $P^3 \sim O$ ligands of complexes **2a,b**. The AB pattern results from two inequivalent phosphorus atoms in **3a,b** and the downfield resonance is in the typical range of $\eta^2(O,P)$-coordinated ether-phosphine ligands [3]. The medium intensity absorptions between 907–928 and 1225–1243 cm^{-1} in the IR spectra of **2a**, **3a** and **2b**, **3b** are attributed to $\nu_{as}(CS_2)$ and $\delta(HCS)$ of the bidentate dithioformato ligand [14]. In the $^{13}C\{^1H\}$ NMR spec-

trum of a mixture of **2a** and **3a** two singlets at lowest field are attributed to the carbon atoms of the dithioformato groups [14]. The relatively upfield resonance of the two singlets is assigned to the carbon atom of the dithioformato group of **2a** and it is consistent with a higher electron density at ruthenium in **2a**. Because of the low yield of complex **2b**, a mixture of **2b** and **3b** shows only one singlet at lowest field in the $^{13}C\{^1H\}$ NMR spectrum, attributed to the carbon atom of the dithioformato group of **3b**.

Supposedly the formation of **2a,b** and **3a,b** proceeds via the intermediates **A** and **B**, in which carbon disulfide is π-bonded to the ruthenium center [15]. This addition either requires an Ru–O bond cleavage or an O,P ligand dissociation in **1a,b** to give **A** and **B** respectively. Subsequently, an insertion of CS_2 into the Ru–H bond follows to give the dithioformato complexes mentioned above.
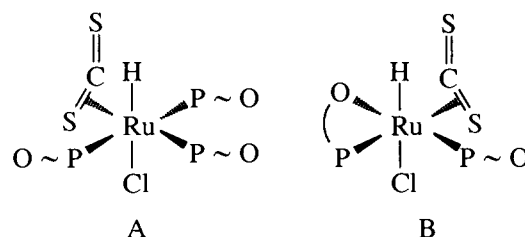
In order to know how the complexes **2a,b** and **3a,b** are related to each other, the following experiments have been carried out in the case of **2a** and **3a**. Mixtures of the compounds were reacted with a hundred-fold excess of carbon disulfide in CH_2Cl_2 for two days, and
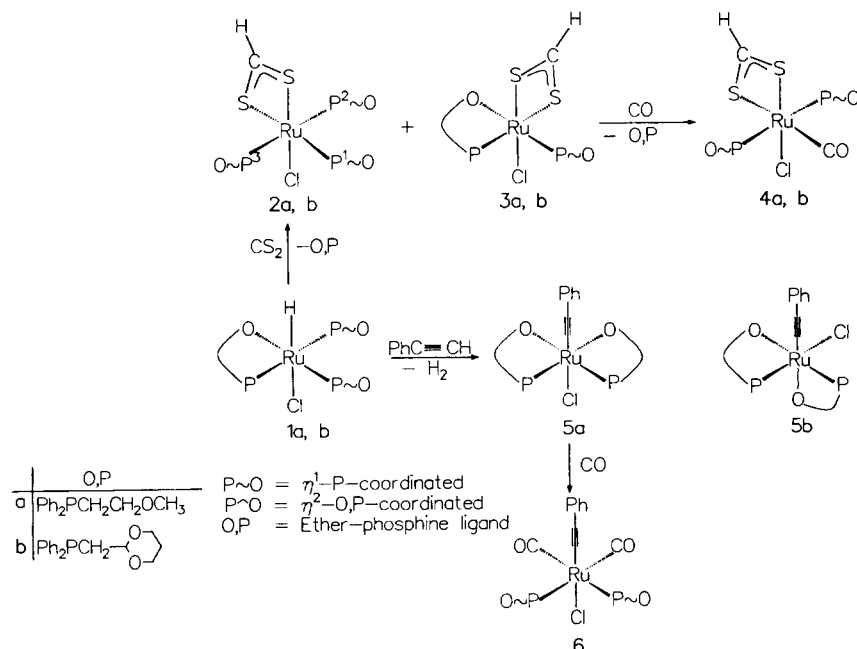
Scheme 1.

the ratio of the complexes did not change. Within 2 h even in refluxing THF the mentioned ratio was formed again. Upon treatment of the obtained 4:3 mixture of **2a** and **3a** with a two-fold excess of $Ph_2PCH_2CH_2OCH_3$ in refluxing toluene for 1 h, the ratio changed to 5:1. To sum up these findings, it can be said that **2a** is formed from **3a** and $Ph_2PCH_2CH_2OCH_3$; but an ether-phosphine dissociation from **2a** to give **3a** does not occur.

To confirm the insertion of CS_2 into the Ru–H bond, complex **2a** was characterized by X-ray diffraction analysis. The ORTEP diagram with atom labeling is shown in Fig. 1. Both sulfur atoms of the incoming CS_2 molecule are coordinated to the ruthenium metal.

The distorted octahedral geometry around the metal atom is due to a small S(1)–Ru–S(2) angle of 70.98(4)° in **2a** (Table 4). This angle is approximately equal to the corresponding value of 69.83(5)° found in $Os(\eta^2\text{-}S_2CH)(P^iPr_3)_3(CO)Cl$ [15]. The two Ru–S bond lengths are significantly different, which is caused by the different *trans*-directing influence of the *trans*-positioned phosphine and chlorine in **2a**.

Interestingly, the action of carbon disulfide on the corresponding tris(triphenylphosphine)ruthenium complex $RuClH(PPh_3)_3$, according to the $^{31}P\{^1H\}$ and $^{31}C\{^1H\}$ NMR spectra, affords more than ten products. Compared with the above-mentioned system this reaction proceeds completely unselectively.

3.2. Carbonylation of complexes 2 and 3 to form the complexes Ru(CO)Cl(P ~ O)₂(η²-S₂CH) (4a,b)

Mixtures of **2a**, **3a** and **2b**, **3b** respectively were allowed to react with carbon monoxide in CH_2Cl_2 to give yellow air-stable products which were identified as

the complexes $Ru(CO)Cl(P \sim O)_2(\eta^2\text{-}S_2CH)$ (**4a,b**). Upon this reaction, not only was one of the ether-phosphine ligands in **2a,b** substituted by carbon monoxide, but also the Ru–O bond of **3a,b** was cleaved to form the carbonylation products **4a,b**. Because of the weaker Ru–O bond of the cyclic ether-phosphine ligand [3a], the rate of formation of **4b** was faster than that of **4a**. **4a** and **4b** are easily soluble in polar, but insoluble in nonpolar, solvents. In the mass spectra of **4a,b**, the molecular ion along with the [M⁺–CO] peak are detected with highest intensity. The IR spectra show one strong carbonyl stretching band at 1946 cm⁻¹ for **4a** and 1947 cm⁻¹ for **4b**. At lowest field one triplet with a small ^4J(PH) coupling constant was found in the ^1H NMR spectra for **4a,b**, which is characteristic of two *trans*-phosphine ligands [16]; it is attributed to the proton of the dithioformato group. Owing to the coupling with two equivalent P atoms, the $^{13}C\{^1H\}$ NMR spectra of **4a** and **4b** reveal two triplets at lowest field, which are assigned to the carbon atoms of the dithioformato ligand and the terminal carbonyl group respectively.

The structure of complex **4a** was determined by X-ray crystal structure analysis to ensure the geometry and nature of the carbonylation reaction. An ORTEP plot of **4a** is shown in Fig. 2. The ruthenium–carbon bond length (Ru(1)–C(31) 1.880(4) Å) in **4a** is shorter than the corresponding Ru–CO distance (2.064(17) Å) in cis-$Ru(CO)Cl(PPh_3)_2(\eta^2\text{-}S_2CH)$ [16], which can be explained by the replacement of the chloride with the better σ-donating dithioformato group in **4a**. The Ru–P distances and that of Ru–Cl (Table 4) in **4a** are identical with those in cis-$Ru(CO)Cl(PPh_3)_2(\eta^2\text{-}S_2CH)$ (Ru–P 2.396(2) and 2.398(2) Å; Ru–Cl 2.421(3) Å). These bond lengths are in the expected range [17].
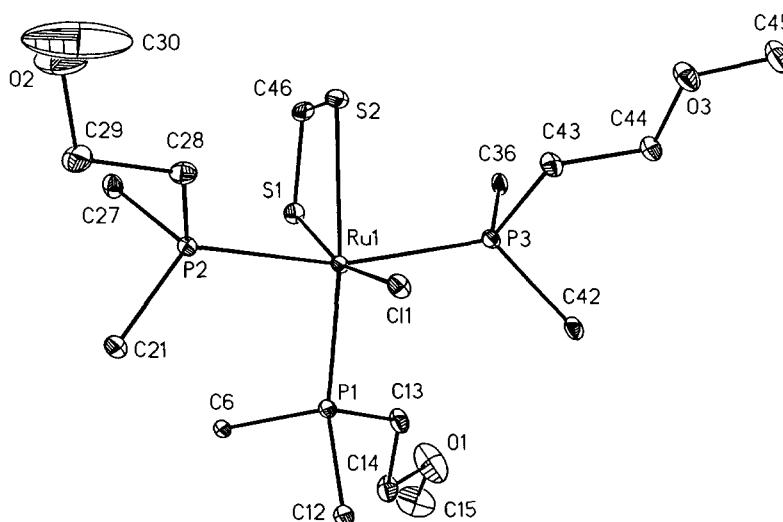

Fig. 1. ORTEP diagram of complex $RuCl(P \sim O)_3(\eta^2\text{-}S_2CH)$ (**2a**). The phenyl groups are omitted for clarity.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for **4a**

Atom	x	y	z	U_{eq}
Ru(1)	519(1)	2192(1)	3975(1)	21(1)
Cl(1)	−61(1)	833(1)	3707(1)	43(1)
P(2)	2457(1)	1853(1)	4024(1)	22(1)
P(1)	−1458(1)	2441(1)	3924(1)	24(1)
S(1)	−11(1)	2532(1)	2444(1)	60(1)
S(2)	890(1)	3527(1)	3841(1)	46(1)
O(1)	−4537(2)	1355(2)	2656(2)	48(1)
O(2)	2776(3)	125(2)	2400(2)	53(1)
O(3)	1397(2)	2273(2)	5870(2)	48(1)
C(1)	−2596(3)	3712(2)	2936(3)	39(1)
C(2)	−2937(4)	4492(3)	2812(3)	54(1)
C(3)	−2630(5)	5009(3)	3470(4)	62(1)
C(4)	−1947(5)	4771(3)	4267(3)	60(1)
C(5)	−1599(4)	3995(2)	4405(3)	43(1)
C(6)	−1943(3)	3457(2)	3747(2)	29(1)
C(7)	−2613(3)	2537(2)	5192(2)	32(1)
C(8)	−2863(3)	2270(2)	5920(2)	36(1)
C(9)	−2285(3)	1621(2)	6354(2)	40(1)
C(10)	−1471(3)	1233(2)	6065(3)	39(1)
C(11)	−1228(3)	1490(2)	5335(2)	33(1)
C(12)	−1795(3)	2151(2)	4900(2)	27(1)
C(13)	−2541(3)	1888(2)	3092(2)	34(1)
C(14)	−3813(3)	1961(3)	3093(3)	52(1)
C(15)	−4822(5)	1395(4)	1773(3)	72(2)
C(16)	3760(3)	3039(2)	5026(2)	34(1)
C(17)	4507(4)	3679(2)	5211(3)	42(1)
C(18)	4949(3)	3977(2)	4590(3)	44(1)
C(19)	4647(4)	3638(2)	3796(3)	41(1)
C(20)	3910(3)	2994(2)	3609(2)	32(1)
C(21)	3462(3)	2688(2)	4230(2)	25(1)
C(22)	2613(3)	687(2)	5261(2)	34(1)
C(23)	3209(4)	172(2)	5890(3)	40(1)
C(24)	4422(4)	134(2)	6138(2)	37(1)
C(25)	5033(3)	621(2)	5756(2)	36(1)
C(26)	4442(3)	1140(2)	5133(2)	31(1)
C(27)	3220(3)	1182(2)	4876(2)	25(1)
C(28)	2706(3)	1393(2)	3080(2)	31(1)
C(29)	2230(4)	558(3)	2922(3)	47(1)
C(30)	2358(5)	324(3)	1555(3)	56(1)
C(31)	1048(3)	2234(2)	5171(2)	33(1)
C(32)	429(4)	3437(3)	2809(4)	64(2)

Table 4

Selected interatomic distances ($\mathring{A}$) and angles (°) for **2a** and **4a**

Complex **2a**		Complex **4a**	
Selected bond lengths ($\mathring{A}$)			
Ru(1)–S(1)	2.325(1)	Ru(1)–S(2)	2.355(1)
Ru(1)–S(2)	2.460(1)	Ru(1)–S(1)	2.478(1)
Ru(1)–P(1)	2.352(1)	Ru(1)–C(31)	1.880(4)
Ru(1)–P(2)	2.392(1)	Ru(1)–P(1)	2.388(1)
Ru(1)–P(3)	2.412(1)	Ru(1)–P(2)	2.376(1)
Ru(1)–Cl(1)	2.482(1)	Ru(1)–Cl(1)	2.434(1)
C(46)–S(1)	1.667(5)	C(32)–S(2)	1.630(6)
C(46)–S(2)	1.691(5)	C(32)–S(1)	1.688(7)
Selected bond angles (°)			
S(1)–Ru(1)–S(2)	70.98(4)	S(1)–Ru(1)–S(2)	70.88(5)
S(1)–Ru(1)–Cl(1)	166.86(4)	S(2)–Ru(1)–Cl(1)	164.90(4)
P(2)–Ru(1)–P(3)	162.04(4)	P(1)–Ru(1)–P(2)	176.10(3)
P(1)–Ru(1)–S(2)	161.76(5)	C(31)–Ru(1)–S(1)	163.68(13)
C(46)–S(2)–Ru(1)	86.1(2)	C(32)–S(1)–Ru(1)	84.2(2)
C(46)–S(1)–Ru(1)	91.1(2)	C(32)–S(2)–Ru(1)	89.6(2)
S(1)–C(46)–S(2)	111.8(3)	S(1)–C(32)–S(2)	115.4(3)
		Ru(1)–C(31)–O(3)	177.2(3)

3.3. Preparation of the acetylide–ruthenium complexes $RuCl(P \cap O)_2(C \equiv CPh)$ (5a,b)

Compared with the bis(chelate)ruthenium complexes $Cl_2Ru(P \cap O)_2$ [18], the starting compounds $RuClH(P \cap O)(P \sim O)_2$ (**1a,b**) show a different behavior toward phenylacetylene. Instead of the formation of η^1-vinylidene complexes, hydrogen is evolved and the acetylide complexes $RuCl(P \cap O)_2(C \equiv CPh)$ (**5a,b**) are formed.

5a and **5b** are obtained in high yields as yellow air-stable products which are soluble in dichloromethane but insoluble in nonpolar solvents. The FAB mass spectra show parent peaks corresponding to the molecular masses of **5a** and **5b**. The IR spectra include a strong band at 2064 cm^{-1} for **5a** and 2065 cm^{-1} for **5b**, which can be assigned to the C≡C stretching mode of the acetylide moiety [19]. In the $^{31}P\{^1H\}$ NMR spectrum of **5a** only one singlet appears, which indicates the cis-position of the two chemically equivalent η^2(O,P)-

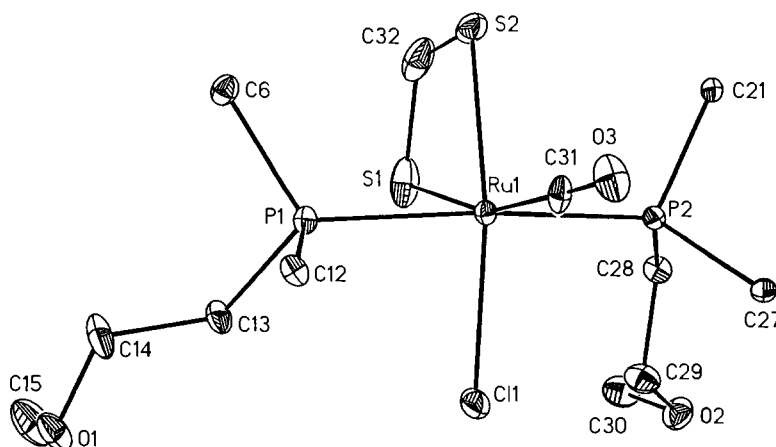Fig. 2. ORTEP diagram of complex $Ru(CO)Cl(P \sim O)_2(\eta^2\text{-}S_2CH)$ (**4a**). The phenyl groups are omitted for clarity.

chelated ether-phosphines. Interestingly, the ^{31}P{^{1}H} NMR spectrum of **5b** shows an AB pattern in the typical range of η^2(O,P)-coordinated O,P ligands [3a]. It is attributed to the unsymmetric geometry of **5b** caused by the steric hindrance of the cyclic ether-phosphines. The ^{13}C{^{1}H} NMR spectra of **5a** and **5b** reveal two broad singlets at δ 110.4 and 108.6 for **5a** and δ 104.7 and 104.2 for **5b**, which are assigned to the carbon atoms of the acetylide moieties [20]. According to the literature [20], the formation of **5a** and **5b** may be due to the oxidative addition of PhC≡CH to the ruthenium metal, or an acid-base reaction between the hydride and PhC≡CH followed by a reductive elimination of H$_2$.

3.4. Carbonylation of complex 5a to form complex RuCl(CO)₂(P ~ O)₂(C≡CPh) (6)

In previous work [1a,21] we investigated the carbonylation of RuCl$_2$(P ∩ O)$_2$ leading to the cleavage of two Ru–O bonds to give the all-*trans*-RuCl$_2$(CO)$_2$(P ~ O)$_2$ product. Although the geometry of RuCl(P ∩ O)$_2$(C≡CPh) (**5a**) is comparable with that of RuCl$_2$(P ∩ O)$_2$, the carbonylation of **5a** results in the complex RuCl(CO)$_2$(P ~ O)$_2$(C≡CPh) (**6**) with a *cis*-arrangement of the carbonyl and phosphine ligands (Scheme 1). Compound **6** is a pale yellow air-stable complex which is soluble in dichloromethane but insoluble in nonpolar solvents. The FAB mass spectrum of **6** shows a base peak corresponding to [M–CO]$^+$. Two strong terminal carbonyl stretching bands in the IR spectrum of **6** display the *cis*-position of the two molecules. One medium IR absorption at 2047 cm^{-1} and two broad singlets at δ 113.4 and 110.2 in the ^{13}C{^{1}H} NMR spectrum confirm the acetylide moiety in complex **6**. The ^{31}P{^{1}H} NMR spectrum of **6** exhibits one resonance, indicating the *cis*-position of the two equivalent η^1(P)-coordinated ether-phosphines [22].

3.5. Chloride abstraction from complex Ru(CO)Cl(P ~ O)₂(η²-S₂CH) (4a) to form the complex [Ru(CO)(P ∩ O)(P ~ O)(η²-S₂CH)][BF₄] (7)

η^2(O,P)-chelated complexes of the type [Cp*Ru(L)-(P ∩ O)][BPh$_4$] (Cp* = η^5-C$_5$Me$_5$; L = CO, P(OEt)$_3$) [22] have been obtained by chloride abstraction from

Cp*Ru(L)(P ~ O)Cl with NaBPh$_4$ in CH$_2$Cl$_2$. The rate of this reaction depends on the basicity of the metal [23]. The employment of NaBPh$_4$ to remove Cl$^-$ from **4a** was not successful. Obviously, the strong electron withdrawing properties of the carbonyl ligand and the weak electron donating function of the dithioformato group in **4a** decrease the electron density at the central metal.

However, the intramolecular coordination of the ether moiety in **4a**, which leads to the η^2(O,P)-chelated complex [Ru(CO)(P ∩ O)(P ~ O)(η^2-S$_2$CH)][BF$_4$] (**7**), succeeded with AgBF$_4$ in tetrahydrofuran at room temperature (Scheme 2). Compound **7** was obtained as a yellow oil which decomposed upon exposure to air. The FAB mass spectrum of **7** shows a base peak corresponding to [Ru(CO)(P ∩ O)(P ~ O)(η^2-S$_2$CH)]$^+$, formed by loss of the BF$_4^-$ group. The ^{31}P{^{1}H} NMR spectrum of **7** exhibits an AB pattern resulting from two different coordination modes of the ether-phosphine ligands. The high field doublet occurs in the typical range of an η^1(P)-coordinated ether-phosphine ligand [22], and the downfield doublet reveals an η^2(O,P)-coordinated ether-phosphine. The ^{13}C{^{1}H} NMR spectrum of **7** reveals two broad singlets at lowest field, which are assigned to the carbon atoms of the dithioformato ligand and the terminal carbonyl group respectively. The shift of the absorption of the carbonyl stretching vibration to higher wavelengths in the IR spectrum of **7** is attributed to the cationic character of the metal center.

3.6. Synthesis of complex Ru(CO)(P ~ O)₂(η²-S₂CH)(C≡CPh) (8)

Methods for the synthesis of a series of η^1-vinylidene complexes using CpRuCl(PR$_3$)$_2$ [24] or [Cp*RuCl{η^2(P,O)-^{i}Pr$_2$PCH$_2$CO$_2$CH$_3$}] [25] and 1-alkynes have been reported. Furthermore, the reaction of the cationic η^2(O,P)-chelated ruthenium complex [Cp*Ru(L)(P ∩ O)][BPh$_4$] (Cp* = η^5-C$_5$Me$_5$; L = CO, P(OEt)$_3$, P ~ O) with phenylacetylene yielded the corresponding cationic η^1-vinylidene complexes [4,23]. To explore the reactivity of complex **7**, we studied its behavior towards phenylacetylene.

The unexpected formation of the acetylide complex Ru(CO)(P ~ O)$_2$(η^2-S$_2$CH)(C≡CPh) (**8**) was achieved by the reaction of **7** with phenylacetylene. It is a yellow
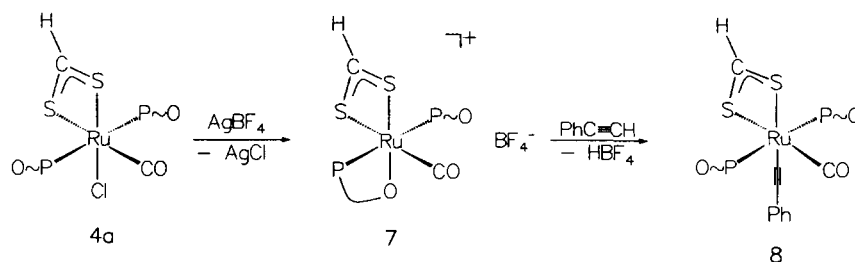
Scheme 2.

air-stable crystalline solid and is soluble in polar solvents like CH_2Cl_2 and $CHCl_3$. The FAB mass spectrum of **8** shows a parent peak which corresponds to the fragment $[Ru(CO)(P \sim O)_2(\eta^2\text{-}S_2CH)(C\equiv CPh)]^+$. The $^{13}C\{^1H\}$ NMR spectrum of **8** indicates one broad singlet and one triplet at δ 113.0 and 110.0 for the acetylide carbon atoms, and the corresponding IR spectrum shows a medium band at 2120 cm^{-1} which is assigned to the $C\equiv C$ bond. Compound **8** reveals a singlet in the $^{31}P\{^1H\}$ NMR spectrum, attributable to the two chemical equivalent η^1(P)-coordinated ether-phosphines. One triplet with a small ^4J(PH) coupling constant at lowest field in the ^1H NMR spectrum of **8** corresponds to the proton of the dithioformato group and is characteristic for the *trans*-position of the two ether-phosphines [16].

3.7. Conclusion

This study describes the chemical behavior of the tris(ether-phosphine)(hydrido)ruthenium(II) complexes RuClH(P ∩ O)(P ∼ O)$_2$ (**1a,b**) provided with different steric-demanding ether-phosphine ligands towards some small molecules. To establish the influence of the steric encumbrance around the ruthenium center, and of the Ru–O bond strength towards incoming substrates, the two ligands $Ph_2PCH_2CH_2OCH_3$ and Ph_2PCH_2-$C_4H_7O_2$ have been employed. One hydrogen and one chlorine ligand and three ether-phosphines with *mer*-position in **1a,b** form the octahedral 18-electron precursors only weakly protected by intramolecular chelation of the ether moiety. Hence, the facile cleavage of one Ru–O bond of the chelated ether-phosphine is used to activate carbon disulfide, phenylacetylene, and carbon monoxide. The reaction of **1b**, which contains the sterically more demanding and weaker Ru–O bonded ligand $Ph_2PCH_2C_4H_7O_2$, with carbon disulfide prefers the formation of the less encumbered dithioformato compound **3b**. Compared with the corresponding triphenylphosphine complex RuClH(PPh$_3$)$_3$, the ether-phosphine complexes **1a,b** react with CS$_2$ to proceed completely selectively. To sum up the results, it can be said that the hindrance of the ether-phosphine ligand in the dithioformato and acetylido products and the weakness of the Ru–O bond respectively are in the order $Ph_2PCH_2C_4H_7O_2 > Ph_2PCH_2CH_2OCH_3$.

Acknowledgements

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